PATENT SPECIFICATION 793,776

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International Classification:—C07c. C08f.

COMPLETE SPECIFICATION.

Esters of Drying Oil Acids with certain Vinyl Polymers.

ERRATA

SPECIFICATION NO. 793,776

Page 2, line 34, *after* "oil" *insert* "acid".

Page 4, line 14, *for* "30-70%" *read* "30-75%".

THE PATENT OFFICE,
20th May, 1958

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copolymers as stabilisers for halogen-containing polymers and as film-forming substances per se in coating compositions.

It has now been found that esters of copolymers of esters such as glycidyl methacrylate and polymerisable vinyl compounds with drying oil acids are extremely useful in the manufacture of coating compositions.

The present invention, therefore, provides an ester of a drying oil acid with a copolymer of glycidyl acrylate or methacrylate and at least one other polymerisable vinyl or vinylidene compound.

The esters may be prepared either by reacting the drying oil acid with the preformed copolymer or by reacting the acid with glycidyl compound and then copolymerising the so formed ester with the other polymerisable vinyl compound. The glycidyl esters may be prepared by any of the known methods. By reacting the drying oil acid with a glycidyl compound better control over and more even distribution of the drying oil vinyl toluene, methacrylonitrile, acrylonitrile, methyl, ethyl, nonyl, lauryl, β-ethoxy ethyl and cyclohexyl methacrylates and the corresponding acrylates.

Copolymers for use in the present invention may readily be prepared by heating the ingredients in the presence of an organic peroxy catalyst such as benzoyl peroxide, tertiary butyl peroxy benzoate, ditertiary butyl peroxide, tertiary alkyl hydroperoxides such as tertiary butyl hydroperoxide or in the presence of a catalyst which functions in a manner similar to a peroxy catalyst such as α,α-diazobutyro-nitrile.

Copolymers most suitable for reacting with a drying oil acid have an epoxide value ranging from 1.3% to 11.26% for glycidyl methacrylate copolymers and from 1.3% to 12.5% for glycidyl acrylate copolymers. The epoxide value is defined as the percentage epoxide oxygen per gramme of resin. The epoxide value depends on the proportion of reactants present.

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THE PATENT OFFICE LONDON

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International Classification:—C07c. C08f.

COMPLETE SPECIFICATION.

Esters of Drying Oil Acids with certain Vinyl Polymers.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to esters of drying oil acids with certain esterifiable vinyl polymers.

It has previously been proposed to copolymerise esters such as glycidyl methacrylate with vinyl compounds such as styrene and vinyl chloride and to use the resulting copolymers as stabilisers for halogen-containing polymers and as film-forming substances per se in coating compositions.

It has now been found that esters of copolymers of esters such as glycidyl methacrylate and polymerisable vinyl compounds with drying oil acids are extremely useful in the manufacture of coating compositions.

The present invention, therefore, provides an ester of a drying oil acid with a copolymer of glycidyl acrylate or methacrylate and at least one other polymerisable vinyl or vinylidene compound.

The esters may be prepared either by reacting the drying oil acid with the preformed copolymer or by reacting the acid with glycidyl compound and then copolymerising the so formed ester with the other polymerisable vinyl compound. The glycidyl esters may be prepared by any of the known methods. By reacting the drying oil acid with a glycidyl compound better control over and more even distribution of the drying oil acid radicles throughout the final polymer molecule can be obtained than is the case when the polymer is obtained by a process involving the esterification of glycerol. In the latter case although the proportions of the reactants in the esterification may be calculated so as to produce say a diglyceride the product will in fact be a mixture containing the other glycerides, and distribution of the drying oil acid radicles in the final polymer will be uneven.

Polymerisable vinyl or vinylidene compounds which may be copolymerised with glycidyl acrylate or methacrylate include, for example, vinyl chloride, vinyl acetate, vinyl toluene, methacrylonitrile, acrylonitrile, methyl, ethyl, nonyl, lauryl, β-ethoxy ethyl and cyclohexyl methacrylates and the corresponding acrylates.

Copolymers for use in the present invention may readily be prepared by heating the ingredients in the presence of an organic peroxy catalyst such as benzoyl peroxide, tertiary butyl peroxy benzoate, ditertiary butyl peroxide, tertiary alkyl hydroperoxides such as tertiary butyl hydroperoxide or in the presence of a catalyst which functions in a manner similar to a peroxy catalyst such as α,α-diazobutyro-nitrile.

Copolymers most suitable for reacting with a drying oil acid have an epoxide value ranging from 1.3% to 11.26% for glycidyl methacrylate copolymers and from 1.3% to 12.5% for glycidyl acrylate copolymers. The epoxide value is defined as the percentage epoxide oxygen per gramme of resin. The epoxide value depends on the proportion of reactants present.

These copolymers are soluble in a wide range of solvents including aromatic hydrocarbons such as xylene and can be esterified with suitable drying oil acids including those derived from linseed oil, sunflower seed oil, tobacco seed oil, soya bean oil, dehydrated castor oil, siccative marine animal oil and tung oil. The esters containing from 30—75% drying oil acids are the most suitable for use in coating compositions.

The esters of the present invention are soluble in a wide range of solvents. Esters which are especially useful are those in which the copolymers are those of glycidyl methacrylate, methyl methacrylate and a methacrylate containing eight or more carbon atoms in the alcoholic group, e.g. nonyl methacrylate. Such esters have good colour and aliphatic solvent toleration.

Solutions of these esters when suitably driered will dry on exposure to air, in a time proportional to the fatty acid content of the ester. Since the products of the present invention are obtained by esterifying a glycidyl compound with drying oil acid, the acid radicles occur in pairs attached to adjacent carbon atoms and consequently better drying characteristics are obtained than is the case when the product is made by a process involving esterification of glycol. In the latter case the esterification takes place preferentially at the terminal hydroxyl groups of the glycerol and consequently the drying oil radicles in a diglyceride are separated.

The esterification of the copolymers may be carried out in the presence or absence of solvents and may be accelerated by means of esterification catalysts such as litharge, caustic soda and organic bases such as quaternary ammonium hydroxides. The order of addition of the reactants and catalysts and the method of addition, i.e. batchwise or continuous uniform addition, can be varied as will be demonstrated in the following Examples in which parts are by weight.

EXAMPLE I.

25.8 parts of glycidyl methacrylate, 80 parts of xylol and 0.66 parts benzoyl peroxide were heated with stirring to reflux temperature. 54.5 parts of methyl methacrylate and 19.28 parts nonyl methacrylate together with 1.34 parts of benzoyl peroxide were added to the refluxing mixture over a period of five hours, the refluxing being continued for a further 1¼ hours after completion of the addition. The mixture was stripped of unreacted monomers under vacuum at 180° C. and the epoxide value of the resulting resin was 2.7%. The resin was a glass-like, yellow coloured, brittle material.

30 parts of this copolymer together with 20 parts of linseed oil fatty acids and 0.5 parts benzyl trimethyl ammonium hydroxide were heated at 190° C. with CO_2 bubbling through the mixture until the acid value of the esterified copolymer was below 15 mgms. KOH/gm.

A solution of this ester thinned to a viscosity of three poise at 25° C. with a 5:1 special boiling petroleum number 6:xylol mixture and driered with 0.1% cobalt gave a hard, dry film, after one hour air drying.

EXAMPLE II.

100 parts of xylol, 30 parts glycidyl methacrylate, 70 parts vinyl toluene, 1 part benzoyl peroxide and 1.5 parts ditertiary butyl peroxide were heated with stirring to reflux temperature for six hours.

To 77.6 parts of this copolymer solution was added 17.5 parts linseed oil acids, 0.35 parts benzyl trimethyl ammonium hydroxide and 35 parts of xylol and the reaction mixture was refluxed for two hours with CO_2 bubbling through the mixture and its resulting acid value being 15 mgms. KOH/gm. The product was light straw coloured and a film prepared as in Example 1 air-dried in 3 hours.

EXAMPLE III.

100 parts of xylol, 30 parts of glycidyl methacrylate, 70 parts of methyl methacrylate, 1 part benzoyl peroxide and 1.5 parts ditertiary butyl peroxide were heated with stirring to reflux temperature for six hours. To 77.6 parts of this copolymer solution was added 17.5 parts of linseed oil acids, 0.35 parts benzyl trimethyl ammonium hydroxide and 35 parts of xylol and the reaction mixture was refluxed for two hours with CO_2 bubbling through the mixture and its resulting acid value being 15 mgms. KOH/gm. The product was light straw coloured and a film prepared as in Example I air-dried in 3½ hours.

EXAMPLE IV.

0.07 parts of hydroquinone, 35.5 parts glycidyl methacrylate, 60 parts of linseed oil acids, 30 parts of xylol and 0.35 parts of benzyl trimethyl ammonium hydroxide were heated to reflux temperature in an atmosphere of CO_2 with stirring. After 1½ hours heating the acid value of the non-volatile product was 10 mgms. KOH/gm. To this reaction mixture was added 55.5 parts methyl methacrylate, 151 parts of xylol, 1 part benzoyl peroxide and 1.5 mls. ditertiary butyl peroxide. Heating at reflux temperature in an atmosphere of CO_2 with stirring was continued for a further four hours. The product was a clear, straw coloured liquid which after stripping off solvent to give a solution of 4 to 5 poise viscosity gave films which when prepared as in Example I airdried in 3 hours.

British Patent 767,476 claims the resinous reaction products of a styrene/glycidyl methacrylate copolymer and an oil acid and we make no claim to such resinous reaction products.

Subject to the foregoing disclaimer, what we claim is:—

1. An ester of a drying oil acid and a copolymer of glycidyl methacrylate or acrylate and at least one other polymerisable vinyl or vinylidene compound.

2. An ester as claimed in Claim 1 containing from 30—75% drying oil acids.

3. An ester as claimed in Claim 2 wherein the drying oil acid comprises drying oil acids derived from linseed oil.

4. An ester as claimed in any of the above claims wherein the copolymer comprises methyl methacrylate and a methacrylate containing eight or more carbon atoms in the alcoholic group.

5. An ester as claimed in any of the above claims wherein the copolymer comprises vinyl toluene, or methyl methacrylate.

6. An ester of a drying oil acid and a copolymer of glycidyl methacrylate or acrylate and another polymerisable vinyl or vinylidene compound prepared substantially as described with reference to any one of the Examples.

7. A process for producing an ester as claimed in any one of the preceding claims wherein the drying oil acid is reacted with glycidyl methacrylate or acrylate and the so-formed ester is further reacted with another polymerisable vinyl or vinylidene compound.

8. A process for producing an ester as claimed in any one of Claims 1 to 5 wherein the drying oil acid is reacted with the copolymer.

9. A process as claimed in Claim 8 in which the copolymer comprises glycidyl methacrylate and has an epoxide value between 11.26% and 1.3% as hereinbefore defined.

10. A process as claimed in Claim 8 in which the copolymer comprises glycidyl acrylate and has an epoxide value between 12.5% and 1.3% as hereinbefore defined.

11. A process for producing an ester of a drying oil acid and a copolymer of glycidyl methacrylate or acrylate and at least one other polymerisable vinyl or vinylidene compound substantially as hereinbefore described with reference to any one of the Examples.

WALTER SCOTT,
Agent for the Applicants.

PROVISIONAL SPECIFICATION.

Esters of Drying Oil Acids with certain Vinyl Polymers.

We, Imperial Chemical Industries Limited, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to esters of drying oil acids with certain esterifiable vinyl polymers.

It has previously been proposed to copolymerise esters such as glycidyl methacrylate with vinyl monomers such as styrene and vinyl chloride and the resulting copolymers have been used as stabilisers for halogen-containing polymers and as film-forming substances per se in coating compositions.

It has now been found that polymers, copolymers and terpolymers of esters such as glycidyl methacrylate can be further esterified with drying oil acids to yield esters which are extremely useful in the manufacture of coating compositions.

The present invention, therefore, provides an ester of at least one siccative drying oil acid with a polymer, copolymer or terpolymer of certain epoxide group containing vinyl monomers.

Glycidyl esters may be prepared by any of the known methods.

Vinyl monomers which may be used in copolymerisation with, for example, glycidyl acrylate or methacrylate include vinyl chloride, vinyl acetate, vinyl toluene, styrene, methacrylonitrile, acrylonitrile, methyl, ethyl, nonyl, lauryl, β-ethoxy ethyl and cyclohexyl methacrylate and the corresponding acrylates.

Polymers and copolymers for use in the present invention may readily be prepared by heating the ingredients in the presence of an organic peroxy catalyst such as benzoyl peroxide, tertiary butyl peroxy benzoate, ditertiary butyl peroxide, tertiary alkyl hydroperoxides such as tertiary butyl hydroperoxide or in the presence of a catalyst which functions as a peroxy catalyst such as α,α-diazobutyronitrile.

The present invention provides for the use of polymers, copolymers and terpolymers of, for example, glycidyl methacrylate with vinyl monomers the epoxide value of the said polymers being variable within the range 11.26% to 1.3%. The epoxide value is defined as the percentage epoxide oxygen per gramme of resin. The epoxide value depends on the proportion of reactants present, the latter figure being the minimum for a satisfactory product in the example using glycidyl methacrylate.

These polymers, copolymers and terpolymers are soluble in a wide range of solvents including aromatic hydrocarbons such as xylene and can be esterified with suitable siccative drying oil acids including those derived from linseed oil, sunflower seed oil, tobacco seed oil, soya bean oil, dehydrated castor oil, siccative marine animal oil and tung oil. The esters containing from 30—70% siccative drying oil acids are the most suitable for use in coating compositions.

The esters of the present invention are soluble in a wide range of solvents. Two types of esters which are especially useful are those prepared from (1) copolymers of glycidyl methacrylate and styrene and (2) copolymers of glycidyl methacrylate, methyl methacrylate and a methacrylate containing eight or more carbon atoms in the alcoholic radical, e.g. nonyl methacrylate, since such esters have good colours and aliphatic solvent toleration.

Solutions of these esters when suitably driered will dry on exposure to air, in a time proportional to the fatty acid content of the ester.

The esterification of the copolymers or polymers may be carried out in the presence or absence of solvents and may be accelerated by means of esterification catalysts such as litharge, caustic soda and organic bases such as quaternary ammonium hydroxides. The order of addition of the reactants and catalysts and the method of addition, i.e. batchwise or continuous uniform addition, influences the properties of the resulting ester.

EXAMPLE I.

25.8 grammes of glycidyl methacrylate, 80 grammes of xylol and 0.66 grammes benzoyl peroxide were heated with stirring to reflux temperature. 54.5 grammes of methyl methacrylate and 19.28 grammes nonyl methacrylate together with 1.34 grammes of benzoyl peroxide were added to the refluxing mixture over a period of five hours, the refluxing being continued for a further 1¼ hours after completion of the addition. The mixture was stripped of unreacted monomers under vacuum at 180° C. and the epoxide value of the resulting resin was 2.7%. The resin was a glass-like, yellow coloured, brittle material.

30 grammes of this polymer together with 20 grammes of linseed oil fatty acids and 0.5 grammes benzyl trimethyl ammonium hydroxide were heated at 190° C. with CO_2 bubbling through the mixture until the acid value of the esterified copolymer was below 15 mgms. KOH/gm.

A solution of this ester thinned to a viscosity of three poise at 25° C. with a 5:1 special boiling petroleum 6-xylol mixture and driered with 0.1% cobalt gave a hard, dry film after one hour air drying.

EXAMPLE II.

29.5 grammes of glycidyil methacrylate, 80 grammes xylol and 1.2 grammes benzoyl peroxide were heated to reflux and over a period of five hours 52 grammes of styrene were uniformly added. Heating was continued and the unreacted monomers stripped as in Example I. The epoxide value of the resulting resin was 3.5%.

55 grammes of this resin and 45 grammes of a whale oil fatty acid were heated with one gramme of benzyl trimethyl ammonium hyldroxide and the esterification continued as in Example I. A film of this resin prepared as in Example I air-dried in one hour ten minutes.

WALTER SCOTT,
Agent for the Applicants.

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